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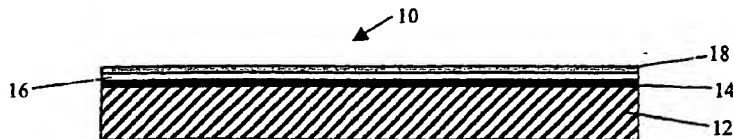
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(54) Title: ENHANCED PURITY OXIDE LAYER FORMATION



(57) Abstract: Methods for producing high quality oxide layers for use in various applications, including high temperature superconducting articles. The oxide layers have complete coverage of grain boundaries, and reduced levels of carbon contamination, while retaining excellent biaxial texture. Particular control over oxidation potential of processing atmosphere and heating steps lead to improved oxide layers.

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Enhanced Purity Oxide Layer Formation

TECHNICAL FIELD

The present invention relates to high temperature superconductors, and more particularly to epitaxial oxide layers and methods of making epitaxial oxide layers.

BACKGROUND

Some high temperature superconductors require well-aligned crystallites with low angle grain boundaries in order to yield high critical currents at relatively high temperatures. For example, thin films consisting of polycrystalline yttrium-barium-copper-oxide superconductors (YBCO) can yield a critical current density exceeding 10^6 A/cm^2 at 77K, self field, when a substantial portion of the local grain boundary misorientations in the film are well below 10° , thereby mitigating the well-known weak link behavior in current transport across boundaries between misoriented regions. This requirement for achieving high critical current densities in polycrystalline films can also be expressed as the YBCO film having a bi-axial texture in which, for example, the c-axis of each crystallite is substantially perpendicular to the film surface and the collective a-axes of all crystallites align in substantially the same direction in the plane of the film surface. To obtain an YBCO thin film with a good (for example, $<< 10^\circ$ for a single crystal substrate) bi-axial texture, it can be deposited in an epitaxial manner on an oxide single crystal such as LaAlO_3 . This is not a commercially viable process for many applications since single crystal substrates cannot be economically produced in very long lengths or large areas. It is therefore more appropriate for industrial purposes to consider the epitaxial deposition of YBCO on a bi-axially textured buffer layer (often an oxide layer), which in turn has been deposited on a flexible metal substrate tape.

The flexible metal substrate can be used to provide a necessary template for texture and mechanical stability during handling and use in applications. Face centered cubic (fcc) metals and some alloys based on fcc metals are especially useful for substrate material, as they can be bi-axially textured using well known rolling deformation and annealing processes. A well-known texture in these metals and alloys is the so called "cube texture", in which the c-axis of the substrate crystallites is

substantially perpendicular to the substrate surface, and the a-axes align primarily along the tape direction. The cube texture can often be made with very low full-width at half-maximum (FWHM) values obtained from X-ray pole figures, an indication of collective alignment of both c- and a-axes of all crystallites. Under controlled rolling and annealing processes, these deformation textured metal tapes possess texture
5 approaching that of single crystals. In practical application of the process, the FWHM texture is less than 10 degrees and more typically less than 8 degrees.

Nickel (Ni) is one fcc metal that can be made into thin substrates with a well-defined cube texture using the rolling and annealing process. Prior work has shown
10 that oxide buffer layers can be deposited on a biaxially textured nickel surface using conditions under which nickel oxide is not stable, but the buffer layer (for example, CeO_2 , Y_2O_3 , Yb_2O_3 , Gd_2O_3 , Eu_2O_3 , SrTiO_3 , LaAlO_3 , GdCuO , or LaNiO_3) is stable, allowing the oxide to inherit the texture of the underlying nickel substrate (that is, epitaxy). A limitation to use of Ni, however, is its ferromagnetic character that may
15 preclude its use in superconducting tape for alternating current (AC) applications such as power transmission cables, motors, and transformers. In addition, Ni is mechanically weak following the typical annealing heat treatment used to form the cube texture.

For these reasons, Ni alloys and other alloys have been developed to make
20 strong, non-magnetic bi-axially textured substrates. These alloys often have alloying elements such as chromium (Cr) or aluminum (Al) that have a tendency to form stable oxides under very low oxygen partial pressure (P_{O_2}). The growth of epitaxial layers on metal or alloy substrates is commonly carried out under P_{O_2} of less than 10^{-17} Torr and 650°C , where the constituent elements such as Cr or Al will form surface oxides.
25 The presence of these surface oxides can inhibit the growth of the epitaxial layers. This can be explained in part due to the fact that the surface oxides are typically randomly oriented on the textured alloy surface and can therefore interfere with a high quality epitaxial buffer layer growth.

One major issue therefore relating to the epitaxial deposition of oxide buffer
30 layers on a bi-axially textured substrate, whether a metal or an alloy, is the control of the oxygen partial pressure, or P_{O_2} . This is true for any buffer deposition technique,

whether it is Physical Vapor Deposition (PVD) by pulsed lasers, sputtering, electron beam, or thermal evaporation, or by a non-vacuum process such as Metal-Organic-Deposition (MOD). The objective is to avoid formation of native oxide films on the surface of the substrate, thereby allowing the deposited buffer layer to nucleate and grow with the appropriate biaxial texture from the substrate surface. Some metals such as silver (Ag) have a natural ability to allow for growth using a great variety in P_{O_2} conditions, but suffer from other disadvantages such as being difficult to texture, having a large coefficient of thermal expansion (CTE), high price, low mechanical strength and the like. Others such as copper (Cu) will easily oxidize. In some metals (for example, Ni), the P_{O_2} can be carefully controlled at the deposition temperature to provide sufficient oxygen to stabilize the buffer layer but insufficient to oxidize the Ni due to basic thermodynamic considerations. Methods to control P_{O_2} below the thermodynamic stability limit for NiO formation have been developed. For this reason, Ni has been established as a good deposition surface for epitaxial oxide layers such as oxides of the rare earth metals (yttria, ytterbia, ceria and the like). As discussed above, however, a pure Ni substrate suffers from other deficiencies that limit its use in various applications.

The typical approach for deposition of the oxide layers includes coating a film of the oxide precursor solution on the substrate, drying excess solvent from the film, thermal decomposition of the oxide precursor under conditions which are reducing with respect to the metal substrate, and heating the film to the desired temperature to form the desired oxide phase. Such procedures can lead to films containing significant and undesirable levels of carbon contamination. Such contamination can lead to the formation of gaseous carbon dioxide in interior portions of the film during subsequent oxide formation. The escaping CO_2 can blister or delaminate the film, to the extreme detriment of performance. The presence of carbon contaminants on or near the surface may also prevent epitaxial growth of additional layers.

In the context of control of oxide layer formation, it would therefore be desirable to provide controlled methods and articles for producing an oxide film from sol gel precursors, completely covering surface grain boundaries, and with reduced

carbon contamination, thereby overcoming the shortcomings associated with the prior art.

SUMMARY

The invention involves the formation of oxide buffer layers, using sol gel seed
5 layers having reduced levels of carbon contamination, as compared to prior art processes. The procedures result in epitaxial formation of subsequently deposited oxide buffer layers, as well as minimal formation of undesired film textures. By controlling the process atmosphere during decomposition of oxide layer precursors, and linking this control to events taking place on the surface on which the layer is
10 formed, high quality film formation is made possible. The invention also involves methods for promoting complete coverage of the grain boundary surfaces of textured substrates by the oxide buffer layer precursor, thereby providing epitaxial growth over the entire surface of the underlying substrate layer.

In one aspect, the invention provides a method of making a oxide layer. The
15 method includes coating a biaxially textured surface with a precursor including rare earth alkoxides and a solvent; removing the solvent; heating the coated surface to a first temperature (between about 80 and about 320 °C, 100 and 300°C, or 100 and 200°C) for a first time (between about 1 and about 60 minutes, 2 and about 45 minutes, or 15 and 45 minutes), which is sufficient to attain substantially complete
20 coverage of grain boundaries of the surface; heating the coated surface, under conditions relatively reducing with respect to the surface (for example, exposure to a gas comprising from about 1 to about 20% hydrogen, or 2 to about 6% hydrogen, and optionally from about 0.5 to about 5% water vapor), to a second temperature (for example, from about 600°C to about 1200°C, or 800°C to about 1150°C), which is
25 sufficient to initiate nucleation of the oxide layer; and modifying the conditions to be more oxidizing with respect to the surface to form the oxide layer. The biaxially textured surface can be a metal or metal alloy substrate which includes nickel, for example. The biaxially textured surface can also be at least one metal oxide buffer layer (such as cerium oxide, gadolinium oxide; for example, CeO₂, Y₂O₃, Yb₂O₃,
30 Gd₂O₃, Eu₂O₃, SrTiO₃, LaAlO₃, GdCuO, or LaNiO₃) coating a metal or metal alloy substrate.

In another aspect, the invention provides an article formed according to the method described above.

In yet another aspect, the invention provides a coated biaxially textured surface including grains and grain boundaries, where the surface is coated with an oxide layer, wherein the coating takes place with a dry process gas, and where the degree of grain coating and the degree of grain boundary coating is substantially the same, as detected by scanning electron microscopy. Less than about 10%, less than about 5%, or less than about 1% of the grain boundaries are not coated with an oxide layer. At least about 95%, or at least about 98% of the surface is coated with a desired texture. The carbon content of the oxide layer is reduced relative to the carbon content of the oxide layer produced without wet process gas.

As used herein, "biaxial" means that the crystal grains in the substrate or film are in close alignment with both a direction perpendicular to the surface of the film and a direction in the plane of the film. Biaxial texturing allows for the production of high current densities in the superconducting film. This biaxial texturing minimizes the weak link effects of high angle grain boundaries allowing the achievement of very high critical current densities in these films at typical device operating conditions.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

DESCRIPTION OF DRAWINGS

Fig. 1 is an illustration of an article according to a particular embodiment of the invention.

Fig. 2 is an X-ray diffraction pattern of a film prepared according to a process known to the prior art.

Fig. 3 is a plot of the stabilities of copper oxide and nickel oxide as a function of oxygen pressure and temperature.

Fig. 4 is an X-ray diffraction pattern of a film prepared according to a process known in the prior art.

Fig. 5 is a pole diagram of a Gd_2O_3 oxide layer.

Fig. 6 is a scanning electron micrograph of a film prepared according to a process known to the prior art.

Fig. 7 is a scanning electron micrograph of a film prepared according to a particular embodiment of the invention.

Fig. 8 is a Rutherford backscattering analysis of a film containing carbon contamination (curve A), and a film prepared according to inventive methods, with reduced carbon contamination (curve B).

Like reference symbols in the various drawings indicate like elements.

DETAILED DESCRIPTION

The invention will be primarily described in connection with the formation of epitaxial oxide buffer layers by means of solutions deposited onto a deformation textured nickel (Ni) surface. This embodiment is intended to be for purposes of illustration and does not limit the scope of the invention, which is determined by the claims and their equivalents. It will be apparent that other epitaxial layers and other intermediate or transient layer materials can be deposited on other substrate alloys. For example, epitaxial oxide buffer layers can also be made by deposition on copper-nickel, nickel-chromium, or nickel-tungsten alloy substrates.

The deposition of oxide films on substrates via solution-based processes is widely used. A wide range of precursor materials can be used for the coating fluid. A common approach is based on metal alkoxide solution chemistries. The advantages of this approach include the ability to deposit uniform coatings over large area
5 substrates using fast coating processes (such as dip coating, web coating, spin coating, and the like), control of stoichiometry, and rapid conversion of the precursor film to the desired oxide phase.

Solution coating processes can be used for deposition of one or a combination of any of the oxide layers on textured substrates; however, they are particularly
10 applicable for deposition of the initial (seed) layer on a textured metal substrate. The role of the seed layer is to provide 1) protection of substrate from oxidation during deposition of the next oxide layer when carried out in an oxidizing atmosphere relative to the substrate (for example, magnetron sputter deposition of yttria-stabilized zirconia from an oxide target); and 2) an epitaxial template for growth of subsequent
15 oxide layers. In order to meet these requirements, the seed layer must grow epitaxially over the entire surface of the metal substrate and be free of any contaminants that may interfere with the deposition of subsequent epitaxial oxide layers.

The deposition of oxide films from metal alkoxide solutions proceeds by
20 coating a metal substrate with an appropriate precursor solution. Appropriate precursor solutions include $\text{RE}(\text{OR})_3$, where RE is a rare earth element (that is, yttrium, europium, ytterbium, gadolinium, and other rare earth elements), and where R can be a C_{1-8} alkyl group, a C_{1-8} alkyl C_{1-8} oxyalkyl group, a C_{1-8} alkanoyloxy group, or any of the above with oxygen atoms present in the carbon chain. Any of the
25 above groups can be branched or unbranched. For example, OR can together constitute methoxy, ethoxy, *n*-propoxy, *iso*-propoxy, *n*-butoxy, *sec*-butoxy, *iso*-butoxy, *tert*-butoxy, acetylacetonate, acetate or other like groups. Precursor solutions can also include mixed alkoxides such as $\text{Sr}(\text{OR})_2\text{Ti}(\text{OR})_4$ or equivalent forms such as LaAlO_3 , LaGdO_3 , and the like. The three OR groups can be all the same or not all the same.

30 Precursor solutions also include solvents, which can belong to general classes of alcohols, aliphatic cyclic and acyclic ethers, hydrocarbons, nitrogenous bases, and

other solvents known to be useful in the preparation of metal alkoxide solutions. For example, ethanol, methanol, propanol isomers, butanol, hexane, tetrahydrofuran, diethylether, pyridine, N-methylpyrrolidine, and similar solvents are useful.

Referring now to Fig. 1, an article 10 formed in accordance with the present invention is illustrated. Article 10 includes substrate 12. Substrate 12 can be formed from a variety of materials.

The substrate can be formed of alloys having one or more surfaces that are biaxially textured (e.g., (113)[211]) or cube textured (e.g., (100)[001] or (100)[011]). The alloys can have a relatively low Curie temperature (e.g., at most about 80K, at most about 40K, or at most about 20K).

In certain embodiments, the substrate is a binary alloy that contains two of the following metals: copper, nickel, chromium, vanadium, aluminum, silver, iron, palladium, molybdenum, gold and zinc. For example, a binary alloy can be formed of nickel and chromium (e.g., nickel and at most 20 atomic percent chromium, nickel and from about five to about 18 atomic percent chromium, or nickel and from about 10 to about 15 atomic percent chromium). As another example, a binary alloy can be formed of nickel and copper (e.g., copper and from about five to about 45 atomic percent nickel, copper and from about 10 to about 40 atomic percent nickel, or copper and from about 25 to about 35 atomic percent nickel). A binary alloy can further include relatively small amounts of impurities (e.g., less than about 0.1 atomic percent of impurities, less than about 0.01 atomic percent of impurities, or less than about 0.005 atomic percent of impurities).

In some embodiments, the substrate contains more than two metals (e.g., a ternary alloy or a quaternary alloy). In these embodiments the alloy can contain one or more oxide formers (e.g., Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb and/or La, with Al being the preferred oxide former), as well as two of the following metals: copper, nickel, chromium, vanadium, aluminum, silver, iron, palladium, molybdenum, gold and zinc. The alloys can contain at least about 0.5 atomic percent oxide former (e.g., at least about one atomic percent oxide former, or at least about two atomic percent oxide former) and at most

about 25 atomic percent oxide former (e.g., at most about 10 atomic percent oxide former, or at most about four atomic percent oxide former). For example, the alloy can include an oxide former (e.g., at least about 0.5 aluminum), from about 25 atomic percent to about 55 atomic percent nickel (e.g., from about 35 atomic percent to about 55 atomic percent nickel, or from about 40 atomic percent to about 55 atomic percent nickel) with the balance being copper. As another example, the alloy can include an oxide former (e.g., at least about 0.5 atomic aluminum), from about five atomic percent to about 20 atomic percent chromium (e.g., from about 10 atomic percent to about 18 atomic percent chromium, or from about 10 atomic percent to about 15 atomic percent chromium) with the balance being nickel. The alloys can include relatively small amounts of impurities (e.g., less than about 0.1 atomic percent of impurities, less than about 0.01 atomic percent of impurities, or less than about 0.005 atomic percent of impurities).

An alloy can be produced by, for example, combining the constituents in powder form, melting and cooling or, for example, by diffusing the powder constituents together in solid state. The alloy can then be formed by deformation texturing (e.g., annealing and rolling, swaging, extrusion and/or drawing) to form a textured surface (e.g., biaxially textured or cube textured). Alternatively, the alloy constituents can be stacked in a jelly roll configuration, and then deformation textured. In some embodiments, a material with a relatively low coefficient of thermal expansion (e.g., Nb, Mo, Ta, V, Cr, Zr, Pd, Sb, NbTi, an intermetallic such as NiAl or Ni₃Al, or mixtures thereof) can be formed into a rod and embedded into the alloy prior to deformation texturing.

These methods are described in commonly owned U.S. Patent Application No. 09/283,775, filed March 31, 1999, and entitled "Alloy Materials;" commonly owned U.S. Patent Application No. 09/283,777, filed March 31, 1999, and entitled "Alloy Materials;" PCT Publication No. WO 99/17307, published on April 8, 1999, and entitled "Substrates with Improved Oxidation Resistance;" and PCT Publication No. WO 99/16941, published on April 8, 1999, and entitled "Substrates for Superconductors," all of which are hereby incorporated by reference.

Substrate 12 can be formed by various techniques. Substrate 12 is preferably formed using a process to induce texturing. In preferred embodiments, texture can be induced in the metallic substrate 12 through deformation texturing ("DeTex").

5 In some embodiments, stable oxide formation can be mitigated until a first epitaxial (for example, buffer) layer is on the biaxially textured alloy surface. Intermediate layers suitable for use in the present invention include those epitaxial metal or alloy layers that do not form surface oxides when exposed to conditions as established by P_{O_2} and temperature required for the initial growth of epitaxial buffer layer films. In addition, the buffer layer acts as a barrier to prevent substrate
10 element(s) from migrating to the surface of the intermediate layer and forming oxides during the initial growth of the epitaxial layer. Absent such an intermediate layer, one or more elements in the substrate would be expected to form thermodynamically stable oxide(s) at the substrate surface which could significantly impede the deposition of epitaxial layers due to, for example, lack of texture in this oxide layer.

15 In some embodiments, the intermediate layer is transient in nature. "Transient," as used herein, refers to an intermediate layer that is wholly or partly incorporated into or with the biaxially textured substrate following the initial nucleation and growth of the epitaxial film. Even under these circumstances, the intermediate layer and biaxially textured substrate remain distinct until the epitaxial
20 nature of the deposited film has been established. The use of transient intermediate layers may be preferred when the intermediate layer possesses some undesirable property, for example, the intermediate layer is magnetic, such as nickel.

Exemplary intermediate metal layers include nickel, gold, silver, palladium, and alloys thereof. Impurities or alloys may include alloys of nickel and/or copper.
25 Epitaxial films or layers deposited on an intermediate layer can include metal oxides, chalcogenides, halides, and nitrides. In preferred embodiments, the intermediate metal layer does not oxidize under epitaxial film deposition conditions.

Care should be taken that the deposited intermediate layer is not completely incorporated into or does not completely diffuse into the substrate before nucleation
30 and growth of the initial buffer layer structure causes the epitaxial layer to be

established. This means that after selecting the metal (or alloy) for proper attributes such as diffusion constant in the substrate alloy, thermodynamic stability against oxidation under practical epitaxial buffer layer growth conditions and lattice matching with the epitaxial layer, the thickness of the deposited metal layer has to be adapted to the epitaxial layer deposition conditions, in particular to temperature.

Deposition of the intermediate metal layer can be done in a vacuum process such as evaporation or sputtering, or by electro-chemical means such as electroplating (with or without electrodes). These deposited intermediate metal layers may or may not be epitaxial after deposition (depending on substrate temperature during deposition), but epitaxial orientation can subsequently be obtained during a post-deposition heat treatment.

As also shown in Fig. 1, intermediate article 10 can include intermediate layer 14. Layer 14 can be formed of a variety of materials as discussed above and can be deposited on substrate 12 using various techniques.

A buffer layer 16 is deposited on layer 14. Buffer layer 16 is preferably an epitaxially grown buffer layer(s) on a DeTex substrate. Layer 16 can be formed of a buffer layer material. Examples of buffer layer materials include metals and metal oxides, such as silver, nickel, TbO_x , GaO_x , CeO_2 , yttria-stabilized zirconia (YSZ), Y_2O_3 , LaAlO_3 , SrTiO_3 , LaNiO_3 , Gd_2O_3 , LaCuO_3 , SrRuO_3 , NdGaO_3 , NdAlO_3 and nitrides as known in the art. A buffer material can be prepared using solution phase techniques, including metalorganic deposition, such as disclosed in, for example, S.S. Shoup et al., J. Am. Cer. Soc., vol. 81, 3019; D. Beach et al., Mat. Res. Soc. Symp. Proc., vol. 495, 263 (1988); M. Paranthaman et al., Superconductor Sci. Tech., vol. 12, 319 (1999); D.J. Lee et al., Japanese J. Appl. Phys., vol. 38, L178 (1999) and M.W. Rupich et al., I.E.E.E. Trans. on Appl. Supercon. vol. 9, 1527.

In certain embodiments, an epitaxial buffer layer can be formed using a low vacuum vapor deposition process (e.g., a process performed at a pressure of at least about 1×10^{-3} Torr). The process can include forming the epitaxial layer using a relatively high velocity and/or focused gas beam of buffer layer material.

The buffer layer material in the gas beam can have a velocity of greater than about one meter per second (e.g., greater than about 10 meters per second or greater than about 100 meters per second). At least about 50% of the buffer layer material in the beam can be incident on the target surface (e.g., at least about 75% of the buffer layer material in the beam can be incident on the target surface, or at least about 90% of the buffer layer material in the beam can be incident on the target surface).

The method can include placing a target surface (e.g., a substrate surface or a buffer layer surface) in a low vacuum environment, and heating the target surface to a temperature which is greater than the threshold temperature for forming an epitaxial layer of the desired material on the target surface in a high vacuum environment (e.g., less than about 1×10^{-3} Torr, such as less than about 1×10^{-4} Torr) under otherwise identical conditions. A gas beam containing the buffer layer material and optionally an inert carrier gas is directed at the target surface at a velocity of at least about one meter per second. A conditioning gas is provided in the low vacuum environment.

The conditioning gas can be contained in the gas beam, or the conditioning gas can be introduced into the low vacuum environment in a different manner (e.g., leaked into the environment). The conditioning gas can react with species (e.g., contaminants) present at the target surface to remove the species, which can promote the nucleation of the epitaxial buffer layer.

The epitaxial buffer layer can be grown on a target surface using a low vacuum (e.g., at least about 1×10^{-3} Torr, at least about 0.1 Torr, or at least about 1 Torr) at a surface temperature below the temperature used to grow the epitaxial layer using physical vapor deposition at a high vacuum (e.g., at most about 1×10^{-4} Torr). The temperature of the target surface can be, for example, from about 25°C to about 800°C (e.g., from about 500°C to about 800°C, or from about 500°C to about 650°C).

The epitaxial layer can be grown at a relatively fast rate, such as, for example, at least about 50 Angstroms per second.

These methods are described in U.S. Patent No. 6,027,564, issued February 22, 2000, and entitled "Low Vacuum Process for Producing Epitaxial Layers," U.S. Patent No. 6,022, 832, issued February 8, 2000, and entitled "Low Vacuum Process

for Producing Superconductor Articles with Epitaxial Layers;" and/or commonly owned U.S. Patent Application No. 09/007,372, filed January 15, 1998, and entitled "Low Vacuum Process for Producing Epitaxial Layers of Semiconductor Material," all of which are hereby incorporated by reference.

5 In some embodiments, a buffer layer can be formed using ion beam assisted deposition (IBAD). In this technique, a buffer layer material is evaporated using, for example, electron beam evaporation, sputtering deposition, or pulsed laser deposition while an ion beam (e.g., an argon ion beam) is directed at a smooth amorphous surface of a substrate onto which the evaporated buffer layer material is deposited.

10 For example, the buffer layer can be formed by ion beam assisted deposition by evaporating a buffer layer material having a rock-salt like structure (e.g., a material having a rock salt structure, such as an oxide, including MgO, or a nitride) onto a smooth, amorphous surface (e.g., a surface having a root mean square roughness of less than about 100 Angstroms) of a substrate so that the buffer layer material has a surface with substantial alignment (e.g., about 13° or less), both in-plane and out-of-
15 plane.

The conditions used during deposition of the buffer layer material can include, for example, a substrate temperature of from about 0°C to about 400°C (e.g., from about room temperature to about 400°C), a deposition rate of from about 1.0
20 Angstrom per second to about 4.4 Angstroms per second, an ion energy of from about 200 eV to about 1200 eV, and/or an ion flux of from about 110 microamperes per square centimeter to about 120 microamperes per square centimeter.

In some embodiments, the substrate is formed of a material having a polycrystalline, non-amorphous base structure (e.g., a metal alloy, such as a nickel
25 alloy) with a smooth amorphous surface formed of a different material (e.g., Si₃N₄).

In certain embodiments, a plurality of buffer layers can be deposited by epitaxial growth on an original IBAD surface. Each buffer layer can have substantial alignment (e.g., about 13° or less), both in-plane and out-of-plane.

These methods are described in PCT Publication No. WO 99/25908, published on May 27, 1999, and entitled "Thin Films Having A Rock-Salt-Like Structure Deposited on Amorphous Surfaces," which is hereby incorporated by reference.

In some embodiments, an epitaxial buffer layer can be deposited by sputtering
5 from a metal or metal oxide target at a high throughput. Heating of the substrate can be accomplished by resistive heating or bias and electric potential to obtain an epitaxial morphology. A deposition dwell may be used to form an oxide epitaxial film from a metal or metal oxide target.

The oxide layer typically present on substrates can be removed by exposure of
10 the substrate surface to energetic ions within a reducing environment, also known as Ion Beam etching. Ion Beam etching can be used to clean the substrate prior to film deposition, by removing residual oxide or impurities from the substrate, and producing an essentially oxide-free preferably biaxially textured substrate surface. This improves the contact between the substrate and subsequently deposited material.
15 Energetic ions can be produced by various ion guns, for example, which accelerate ions such as Ar^+ toward a substrate surface. Preferably, gridded ion sources with beam voltages greater than 150 eV are utilized. Alternatively, a plasma can be established in a region near the substrate surface. Within this region, ions chemically interact with a substrate surface to remove material from that surface, including metal
20 oxides, to produce substantially oxide-free metal surface.

Another method to remove oxide layers from a substrate is to electrically bias the substrate. If the substrate tape or wire is made negative with respect to the anode potential, it will be subjected to a steady bombardment by ions from the gas prior to the deposition (if the target is shuttered) or during the entire film deposition. This ion
25 bombardment can clean the wire or tape surface of absorbed gases that might otherwise be incorporated in the film and also heat the substrate to elevated deposition temperatures. Such ion bombardment can be further advantageous by improving the density or smoothness of the epitaxial film.

Upon formation of an appropriately textured, substantially oxide-free substrate
30 surface, deposition of a buffer layer can begin. One or more buffer layers, each

including a single metal or oxide layer, can be used. In some preferred embodiments, the substrate is allowed to pass through an apparatus adapted to carry out steps of the deposition method of these embodiments. For example, if the substrate is in the form of a wire or tape, the substrate can be passed linearly from a payout reel to a take-up reel, and steps can be performed on the substrate as it passes between the reels.

According to some embodiments, substrate materials are heated to elevated temperatures which are less than about 90% of the melting point of the substrate material but greater than the threshold temperature for forming an epitaxial layer of the desired material on the substrate material in a vacuum environment at the predetermined deposition rate. In order to form the appropriate or matching buffer layer crystal structure and film buffer layer smoothness, high substrate temperatures are generally preferred. Typical lower limit temperatures for the growth of oxide layers on metal are approximately 200°C to 800°C, preferably 500°C to 800°C, and more preferably, 650°C to 800°C. Various well-known methods such as radiative heating, convection heating, and conduction heating are suitable for short (2 cm to 10 cm) lengths of substrate, but for longer (1m to 100 m) lengths, these techniques may not be well suited. Also to obtain desired high throughput rates in a manufacturing process, the substrate wire or tape must be moving or transferring between deposition stations during the process. According to particular embodiments, the substrates are heated by resistive heating, that is, by passing a current through the metal substrate, which is easily scaleable to long length manufacturing processes. This approach works well while instantaneously allowing for rapid travel between these zones. Temperature control can be accomplished by using optical pyrometers and closed loop feedback systems to control the power supplied to the substrate being heated. Current can be supplied to the substrate by electrodes which contact the substrate in at least two different segments of the substrate. For example, if the substrate, in the form of a tape or wire, is passed between reels, the reels themselves could act as electrodes. Alternatively, if guides are employed to transfer the substrate between reels, the guides could act as electrodes. The electrodes could also be completely independent of any guides or reels as well. In some preferred embodiments, current is applied to the tape between current wheels.

In order that the deposition is carried out on tape that is at the appropriate temperature, the metal or oxide material that is deposited onto the tape is desirably deposited in a region between the current wheels. Because the current wheels can be efficient heat sinks and can thus cool the tape in regions proximate to the wheels, material is desirably not deposited in regions proximate to the wheels. In the case of sputtering, the charged material deposited onto the tape is desirably not influenced by other charged surfaces or materials proximate to the sputter flux path. For this reason, the sputter chamber is preferably configured to place components and surfaces which could influence or deflect the sputter flux, including chamber walls, and other deposition elements, in locations distant from the deposition zone so that they do not alter the desired deposition of metal or metal oxide in regions of the tape at the proper deposition temperature.

More details are provided in commonly owned United States Patent Application Serial No. 09/500,701, filed on February 9, 2000, and entitled "Oxide Layer Method," and commonly owned United States Patent Application Serial No. _____, filed on even date herewith, and entitled "Oxide Layer Method," both of which are hereby incorporated by reference in their entirety.

In preferred embodiments, three buffer layers are used. A layer of Y_2O_3 or CeO_2 (e.g., from about 20 nanometers to about 50 nanometers thick) is deposited (e.g., using electron beam evaporation) onto the substrate surface. A layer of YSZ (e.g., from about 0.2 micron to about 1 micron thick, such as about 0.5 micron thick) is deposited onto the surface of the Y_2O_3 or CeO_2 layer using sputtering (e.g., using magnetron sputtering). A CeO_2 layer (e.g., about 20 nanometers thick) is deposited (e.g., using magnetron sputtering) onto the YSZ surface. The surface of one or more of these layers can be chemically and/or thermally conditioned as described herein.

In certain embodiments, the underlying layer (e.g., a buffer layer or a different superconductor layer) can be conditioned (e.g., thermally conditioned and/or chemically conditioned) so that the superconductor layer is formed on a conditioned surface. The conditioned surface of the underlying layer can be biaxially textured (e.g., (113)[211]) or cube textured (e.g., (100)[011] or (100)[011]), have peaks in an X-ray diffraction pole figure that have a full width at half maximum of less than about

20° (e.g., less than about 15°, less than about 10°, or from about 5° to about 10°), be smoother than before conditioning as determined by high resolution scanning electron microscopy or atomic force microscopy, have a relatively high density, have a relatively low density of impurities, exhibit enhanced adhesion to other material
5 layers (e.g., a superconductor layer or a buffer layer) and/or exhibit a relatively small rocking curve width as measured by x-ray diffraction.

“Chemical conditioning” as used herein refers to a process which uses one or more chemical species (e.g., gas phase chemical species and/or solution phase chemical species) to affect changes in the surface of a material layer, such as a buffer
10 layer or a superconductor material layer, so that the resulting surface exhibits one or more of the above noted properties.

“Thermal conditioning” as used herein refers to a process which uses elevated temperature to affect changes in the surface of a material layer, such as a buffer layer or a superconductor material layer, so that the resulting surface exhibits one or more
15 of the above noted properties. Preferably, thermal conditioning occurs in a controlled environment (e.g., controlled gas pressure, controlled gas environment and/or controlled temperature).

Thermal conditioning can include heating the surface of the underlying layer to a temperature at least about 5°C above the deposition temperature or the
20 crystallization temperature of the underlying layer (e.g., from about 15°C to about 500°C above the deposition temperature or the crystallization temperature of the underlying layer, from about 75°C to about 300°C above the deposition temperature or the crystallization temperature of the underlying layer, or from about 150°C to about 300°C above the deposition temperature or the crystallization temperature of
25 the underlying layer). Examples of such temperatures are from about 500°C to about 1200°C (e.g., from about 800°C to about 1050°C). Thermal conditioning can be performed under a variety of pressure conditions, such as above atmospheric pressure, below atmospheric pressure, or at atmospheric pressure. Thermal conditioning can also be performed using a variety of gas environments (e.g., an oxidizing gas
30 environment, a reducing gas environment, or an inert gas environment).

"Deposition temperature" as used herein refers to the temperature at which the layer being conditioned was deposited.

"Crystallization temperature" as used herein refers to the temperature at which a layer of material (e.g., the underlying layer) takes on a crystalline form.

5 Chemical conditioning can include vacuum techniques (e.g., reactive ion etching, plasma etching and/or etching with fluorine compounds, such as BF_3 and/or CF_4). Chemical conditioning techniques are disclosed, for example, in Silicon Processing for the VLSI Era, Vol. 1, eds. S. Wolf and R.N. Tanber, pp. 539-574, Lattice Press, Sunset Park, CA, 1986.

10 Alternatively or additionally, chemical conditioning can involve solution phase techniques, such as disclosed in Metallurgy and Metallurgical Engineering Series, 3d ed., George L. Kehl, McGraw-Hill, 1949. Such techniques can include contacting the surface of the underlying layer with a relatively mild acid solution (e.g., an acid solution containing less about 10 percent acid, less than about two
15 percent acid, or less than about one percent acid). Examples of mild acid solutions include perchloric acid, nitric acid, hydrofluoric acid, hydrochloric acid, acetic acid and buffered acid solutions. In one embodiment, the mild acid solution is about one percent aqueous nitric acid. In certain embodiments, bromide-containing and/or bromine-containing compositions (e.g., a liquid bromine solution) can be used to
20 condition the surface of a buffer layer or a superconductor layer.

This method can be used to form multiple buffer layers (e.g., two, three, four, or more buffer layers), with one or more of the buffer layers having a conditioned surface.

25 The method can also be used to form multiple superconductor layers, with one or more of the superconductor layers having a conditioned surface. For example, a superconductor layer can be formed and then thermally and/or chemically conditioned as described above. An additional superconductor layer can then be formed on the conditioned surface of the first superconductor layer. This process can be repeated as many times as desired.

These methods are described in commonly owned U.S. Provisional Patent Application No. 60/166, 140, filed November 18, 1999, and entitled "Multi-Layer Articles and Methods of Making Same," and commonly owned U.S. Patent Application Serial No. _____, filed on even date herewith, and entitled "Multi-layer Articles and Methods of Making Same," both of which are hereby incorporated by reference.

In some preferred embodiments, the buffer layer is deposited utilizing sol gel deposition methods, as detailed herein. In some other preferred embodiments, the high temperature superconducting layer is deposited utilizing sol gel deposition methods, as detailed herein. In some other preferred embodiments, both the buffer and high temperature superconductor layers are deposited utilizing sol gel deposition methods.

Preferably, layer 18 is a high temperature superconductor (HTS) layer.

In certain embodiments, the superconductor layer can be formed from a precursor composition that has a relatively small amount of free acid. In aqueous solutions, this can correspond to a precursor composition with a relatively neutral pH (e.g., neither strongly acidic nor strongly basic). The precursor composition can be used to prepare multi-layer superconductors using a wide variety of materials which can be used as the underlying layer on which the superconductor layer is formed.

The total free acid concentration of the precursor composition can be less than about 1×10^{-3} molar (e.g., less than about 1×10^{-5} molar or about 1×10^{-7} molar). Examples of free acids that can be contained in a precursor composition include trifluoroacetic acid, acetic acid, nitric acid, sulfuric acid, acids of iodides, acids of bromides and acids of sulfates.

When the precursor composition contains water, the precursor composition can have a pH of at least about 3 (e.g., at least about 5 or about 7).

In some embodiments, the precursor composition can have a relatively low water content (e.g., less than about 50 volume percent water, less than about 35 volume percent water, less than about 25 volume percent water).

In embodiments in which the precursor composition contains trifluoroacetic acid and an alkaline earth metal (e.g., barium), the total amount of trifluoroacetic acid can be selected so that the mole ratio of fluorine contained in the precursor composition (e.g., in the form of trifluoroacetate) to the alkaline earth metal (e.g.,
5 barium ions) contained in the precursor composition is at least about 2:1 (e.g., from about 2:1 to about 18.5:1, or from about 2:1 to about 10:1).

Superconducting articles formed from such precursor compositions can include more than one superconductor layer (e.g., two superconductor layers disposed on each other). The combined thickness of the superconductor layers can be at least
10 about one micron (e.g., at least about two microns, at least about three microns, at least about four microns, at least about five microns, or at least about six microns). The combined critical current density of the superconductor layers can be at least about 5×10^5 Amperes per square centimeter (e.g., at least about 1×10^6 Amperes per square centimeter, or at least about 2×10^6 Amperes per square centimeter).

15 In general, the precursor compositions can be prepared by combining soluble compounds of a first metal (e.g., copper), a second metal (e.g., an alkaline earth metal), and a rare earth metal with one or more desired solvents and optionally water. As used herein, "soluble compounds" of the first, second and rare earth metals refer to compounds of these metals that are capable of dissolving in the solvent(s) contained
20 in the precursor compositions. Such compounds include, for example, salts (e.g., nitrates, acetates, alkoxides, iodides, sulfates and trifluoroacetates), oxides and hydroxides of these metals.

These methods and compositions are described in commonly owned U.S. Provisional Patent Application Serial No. 60/166, 297, filed on November 18, 1999,
25 and entitled "Superconductor Articles and Compositions and Methods for Making Same," and commonly owned U.S. Patent Application No. _____, filed on even date herewith, and entitled "Superconductor Articles and Compositions and Methods for Making Same," both of which are hereby incorporated by reference.

In certain embodiments, a precursor solution is formed of an organic solution
30 containing metal trifluoroacetates prepared from powders of BaCO_3 , $\text{YCO}_3 \cdot 3\text{H}_2\text{O}$ and

Cu(OH)₂CO₃ combined and reacted using methods known to those skilled in the art. For example, the powders can be combined in a 2:1:3 ratio with between 20-30% (5.5-6.0 M) excess trifluoroacetic acid in methyl alcohol and then refluxed (e.g., for approximately four to ten hours) to produce a solution substantially 0.94 M based on copper content.

The precursor solution is then applied to a surface (e.g., a buffer layer surface), such as by spin coating or other techniques known to those skilled in the art.

After application to the surface (e.g., the buffer layer surface), the precursor solution is heat treated. Generally, the solution is heated at a rate of from about 0.5°C per minute to about 10°C per minute in moist oxygen (e.g., having a dew point in the range of from about 20°C to about 75°C) to a temperature in the range of from about 300°C to about 500°C. The coating is then heated for about one hour to a temperature of less than about 860°C (e.g., less than about 810°C) in a moist reducing nitrogen-oxygen gas mixture (e.g., having a composition including from about 0.5% to about 5% oxygen). Optionally, the coating can be further heated to a temperature of from about 860°C to about 950°C for from about five to about 25 minutes. The coating is subsequently heated to a temperature of from about 400°C to about 500°C for at least about eight hours at in dry oxygen. The coating can then be cooled to room temperature in static dry oxygen.

These methods are described in U.S. Patent No. 5,231,074, issued on July 27, 1993, and entitled "Preparation of Highly Textured Oxide Superconducting Films from MOD Precursor Solutions," which is hereby incorporated by reference.

In some embodiments, a metal oxyfluoride is deposited using one or more standard techniques, such as metalorganic solution deposition, metalorganic chemical vapor deposition, reactive evaporation, plasma spray, molecular beam epitaxy, laser ablation, ion beam sputtering, electron beam evaporation, depositing a metal trifluoroacetate coating and decomposing the coating as described herein. Multiple layers of metal oxyfluoride may be deposited.

Other constituent metallic elements of the desired oxide superconductor are also deposited in substantially stoichiometric proportions.

The metal oxyfluoride is converted into an oxide superconductor at a rate of conversion selected by adjusting temperature, vapor pressure of gaseous water or both. For example, the metal oxyfluoride can be converted in a processing gas having a moisture content of less than 100% relative humidity (e.g., less than about 95% relative humidity, less than about 50% relative humidity, or less than about 3% relative humidity) at 25°C to form some oxide superconductor, then completing the conversion using a processing gas having a higher moisture content (e.g., from about 95% relative humidity to about 100% relative humidity at 25°C). The temperature for converting the metal oxyfluoride can be in the range of from about 700°C to about 900°C (e.g., from about 700°C to about 835°C). The processing gas preferably contains from about 1 volume percent oxygen gas to about 10 volume percent oxygen gas.

These methods are described in PCT Publication No. WO 98/58415, published on December 23, 1998, and entitled "Controlled Conversion of Metal Oxyfluorides into Superconducting Oxides," which is hereby incorporated by reference.

In certain embodiments, the preparation of the superconductor layer includes using a precursor composition containing a trifluoroacetate salt of one or more metals and a controlled total water content (e.g., controlled content of liquid water in the precursor composition and controlled content of water vapor in the surrounding environment) present when treating the precursor composition to form an intermediate of the superconductor layer (e.g., a metal oxyfluoride intermediate of the superconductor layer). For example, the precursor composition can have a relatively low water content (e.g., less than about 50 volume percent water, less than about 35 volume percent water, or less than about 25 volume percent water) and/or a relatively high solids content, whereas the surrounding gas environment can have a relatively high vapor pressure of water (e.g., from about 5 Torr to about 50 Torr water, from about 5 Torr to about 30 Torr water, or from about 10 Torr to about 25 Torr water). The superconductor layer intermediate (e.g., metal oxyfluoride intermediate) can be formed in a relatively short period of time (e.g., less than about five hours, less than about three hours, or less than about one hour).

Treating the precursor composition can include heating the precursor composition from an initial temperature (e.g., room temperature) to a temperature of from about 190°C to about 215°C (e.g., about 210°C) at a rate of at least about 5°C per minute (e.g., at least about 8°C per minute, or at least about 10°C per minute) in a water vapor pressure of from about 5 Torr to about 50 Torr water vapor (e.g., from about 5 Torr to about 30 Torr water vapor, or from about 10 Torr to about 25 Torr water vapor). The nominal partial pressure of oxygen can be, for example, from about 0.1 Torr to about 760 Torr.

Heating is then continued to a temperature of from about 220°C to about 290°C (e.g., about 220°C) at a rate of from about 0.05°C per minute to about 0.4°C per minute (e.g., from about 0.1°C per minute to about 0.4°C per minute) in a water vapor pressure of from about 5 Torr to about 50 Torr water vapor (e.g., from about 5 Torr to about 30 Torr water vapor, or from about 10 Torr to about 25 Torr water vapor). The nominal partial pressure of oxygen can be, for example, from about 0.1 Torr to about 760 Torr.

This is followed by heating to about 400°C at a rate of at least about 2°C per minute (e.g., at least about 3°C per minute, or at least about 5°C per minute) in a water vapor pressure of from about 5 Torr to about 50 Torr water vapor (e.g., from about 5 Torr to about 30 Torr water vapor, or from about 10 Torr to about 25 Torr water vapor) to form an intermediate of the superconductor material (e.g., a metal oxyfluoride intermediate). The nominal partial pressure of oxygen can be, for example, from about 0.1 Torr to about 760 Torr.

The intermediate can be heated to form the desired superconductor layer. For example, the intermediate can be heated to a temperature of from about 700°C to about 825°C in an environment containing from about 0.1 Torr to about 50 Torr oxygen and from about 0.1 Torr to about 150 Torr water vapor (e.g., about 12 Torr water vapor) with the balance being, for example, nitrogen and/or argon.

The method can result in a well-ordered superconductor layer (e.g., biaxially textured or cube textured) having a relatively high critical current density (e.g., at least about 5×10^5 Amperes per square centimeter).

These methods are described in commonly owned U.S. Provisional Patent Application Serial No. 60/166,145, filed on November 18, 1999, and entitled "Methods and Compositions for Making a Multi-Layer Article," and commonly owned U.S. Patent Application No. _____, filed on even date herewith, and
5 entitled "Methods and Compositions for Making a Multi-layer Article," both of which are hereby incorporated by reference.

In certain embodiments, a metal oxyfluoride intermediate of a superconductor material can be prepared using a process that involves relatively few temperature ramps (e.g., less than three ramps, such as two ramps).

10 Alternatively or additionally, forming the metal oxyfluoride can include one or more steps in which the temperature is held substantially constant (e.g., constant within about 10°C, within about 5°C, within about 2°C, within about 1°C) for a relatively long period of time (e.g., more than about one minute, more than about five minutes, more than about 30 minutes, more than about an hour, more than about two
15 hours, more than about four hours) after a first temperature ramp to a temperature greater than about room temperature (e.g., at least about 50°C, at least about 100°C, at least about 200°C, at least about 215°C, from about 215°C to about 225°C, about 220°C).

Formation of the metal oxyfluoride intermediate can involve using more than
20 one gas environment (e.g., a gas environment having a relatively high water vapor pressure and a gas environment having a relatively low water vapor pressure) while maintaining the temperature substantially constant (e.g., constant within about 10°C, within about 5°C, within about 2°C, within about 1°C) for a relatively long period of time (e.g., more than about one minute, more than about five minutes, more than
25 about 30 minutes, more than about an hour, more than about two hours, more than about four hours). As an example, in a high water vapor pressure environment, the water vapor pressure can be from about 17 Torr to about 40 Torr (e.g., from about 25 Torr to about 38 Torr, such as about 32 Torr). A low water vapor pressure environment can have a water vapor pressure of less than about 1 Torr (e.g., less than
30 about 0.1 Torr, less than about 10 milliTorr, about five milliTorr).

Generally, the metal oxyfluoride is formed by disposing a composition (e.g., a precursor solution) on a surface (e.g., a substrate surface, a buffer layer surface or a superconductor layer surface) and heating the composition. The methods of disposing the composition on the surface include spin coating, dip coating, web coating and
5 other techniques known in the art.

Typically, in an initial decomposition step, the initial temperature in this step is about room temperature, and the final temperature is from about 215°C to about 225°C using a temperature ramp of 10°C per minute or less. During this step, the partial pressure of water vapor in the nominal gas environment is preferably
10 maintained at from about 17 Torr to about 40 Torr. The partial pressure of oxygen in the nominal gas environment can be maintained at from about 0.1 Torr to about 760 Torr. The temperature and nominal gas environment are then held substantially constant for a relatively long period of time.

After this time period, the gas environment is changed to a relatively dry gas
15 environment (e.g., less than about one Torr water vapor, less than about 0.1 Torr water vapor, less than about 10 milliTor water vapor, five milliTor water vapor) while maintaining the temperature substantially constant. The temperature and nominal gas environment are then held substantially constant for a relatively long period of time.

20 After this time period, the nominal gas environment is maintained substantially constant and heating is continued to a temperature sufficient to form the metal oxyfluoride intermediate (e.g., about 400°C). This step is preferably performed using a temperature ramp of 10°C per minute or less.

The metal oxyfluoride intermediate can then be heated to form the desired
25 superconductor layer. Typically, this step is performed by heating to a temperature of from about 700°C to about 825°C. During this step, the nominal gas environment typically can contain from about 0.1 Torr to about 50 Torr oxygen and from about 0.1 Torr to about 150 Torr (e.g., about 12 Torr) of water vapor with the balance being nitrogen and/or argon. Preferably, the metal oxyfluoride intermediate has a relatively
30 low defect density.

These methods are described in commonly owned U.S. Patent Application Serial No. _____, filed on even date herewith, and entitled "Methods of Making A Superconductor," which is hereby incorporated by reference.

5 In certain embodiments, the superconducting layer can be formed from solid-state, or semi solid state, precursor materials deposited in the form of a dispersion. These precursor compositions allow for example the substantial elimination of BaCO_3 formation in final YBCO superconducting layers, while also allowing control of film nucleation and growth.

Two general approaches are presented for the formulation of precursor
10 compositions. In one approach, the cationic constituents of the precursor composition are provided in components taking on a solid form, either as elements, or preferably, compounded with other elements. The precursor composition is provided in the form of ultrafine particles which are dispersed so that they can be coated onto and adhere onto the surface of a suitable substrate, intermediate-coated substrate, or buffer-coated
15 substrate. These ultrafine particles can be created by aerosol spray, by evaporation or by similar techniques which can be controlled to provide the chemical compositions and sizes desired. The ultrafine particles are less than about 500 nm, preferably less than about 250 nm, more preferably less than about 100 nm and even more preferably less than about 50 nm. In general, the particles are less than about 50% the thickness
20 of the desired final film thickness, preferably less than about 30% most preferably less than about 10% of the thickness of the desired final film thickness. For example, the precursor composition can comprise ultrafine particles of one or more of the constituents of the superconducting layer in a substantially stoichiometric mixture, present in a carrier. This carrier comprises a solvent, a plasticizer, a binder, a
25 dispersant, or a similar system known in the art, to form a dispersion of such particles. Each ultrafine particle can contain a substantially compositionally uniform, homogeneous mixture of such constituents. For example, each particle can contain BaF_2 , and rare-earth oxide, and copper oxide or rare earth/barium/copper oxyfluoride in a substantially stoichiometric mixture. Analysis of such particles would desirably
30 reveal a rare-earth:barium:copper ratio as substantially 1:2:3 in stoichiometry, with a

fluorine:barium ratio of substantially 2:1 in stoichiometry. These particles can be either crystalline, or amorphous in form.

In a second approach, the precursor components can be prepared from elemental sources, or from a substantially stoichiometric compound comprising the desired constituents. For example, evaporation of a solid comprising a substantially stoichiometric compound of desired REBCO constituents (for example, $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$) or a number of solids, each containing a particular constituent of the desired final superconducting layer (for example, Y_2O_3 , BaF_2 , CuO) could be used to produce the ultrafine particles for production of the precursor compositions. Alternatively, spray drying or aerosolization of a metalorganic solution comprising a substantially stoichiometric mixture of desired REBCO constituents could be used to produce the ultrafine particles used in the precursor compositions. Alternatively, one or more of the cationic constituents can be provided in the precursor composition as a metalorganic salt or metalorganic compound, and can be present in solution. The metalorganic solution can act as a solvent, or carrier, for the other solid-state elements or compounds. According to this embodiment, dispersants and/or binders can be substantially eliminated from the precursor composition. For example, the precursor composition can comprise ultrafine particles of rare-earth oxide and copper oxide in substantially a 1:3 stoichiometric ratio, along with a solublized barium-containing salt, for example, barium-trifluoroacetate dissolved in an organic solvent, such as methanol.

If the superconducting layer is of the REBCO type, the precursor composition can contain a rare earth element, barium, and copper in the form of their oxides; halides such as fluorides, chlorides, bromides and iodides; carboxylates and alcoholates, for example, acetates, including trihaloacetates such as trifluoroacetates, formates, oxalates, lactates, oxyfluorides, propylates, citrates, and acetylacetonates, and, chlorates and nitrates. The precursor composition can include any combination of such elements (rare earth element, barium, and copper) in their various forms, which can convert to an intermediate containing a barium halide, plus rare earth oxyfluoride and copper(oxyfluoride) without a separate decomposition step or with a decomposition step that is substantially shorter than that which may be required for

precursors in which all constituents are solubilized, and without substantial formation of BaCO_3 , and which can subsequently be treated using high temperature reaction processes to yield an epitaxial REBCO film with T_c of no less than about 89K, and J_c greater than about $500,000 \text{ A/cm}^2$ at a film thickness of 1 micron or greater. For example, for a $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$ superconducting layer, the precursor composition could contain barium halide (for example, barium fluoride), yttrium oxide (for example, Y_2O_3), and copper oxide; or yttrium oxide, barium trifluoroacetate in a trifluoroacetate/methanol solution, and a mixture of copper oxide and copper trifluoroacetate in trifluoroacetate/methanol. Alternatively, the precursor composition could contain Ba-trifluoroacetate, Y_2O_3 , and CuO . Alternatively, the precursor composition could contain barium trifluoroacetate and yttrium trifluoroacetate in methanol, and CuO . Alternatively, the precursor composition could contain BaF_2 and yttrium acetate and CuO . In some preferred embodiments, barium-containing particles are present as BaF_2 particles, or barium fluoroacetate. In some embodiments the precursor could be substantially a solubilized metalorganic salt containing some or all of the cation constituents, provided at least a portion of one of the compounds containing cation constituents present in solid form. In certain embodiments, the precursor in a dispersion includes a binder and/or a dispersant and/or solvent(s).

The precursor compositions can be applied to substrate or buffer-treated substrates by a number of methods, which are designed to produce coatings of substantially homogeneous thickness. For example, the precursor compositions can be applied using spin coating, slot coating, gravure coating, dip coating, tape casting, or spraying. The substrate is desirably uniformly coated to yield a superconducting film of from about 1 to 10 microns, preferably from about 1 to 5 microns, more preferably from about 2 to 4 microns.

More details are provided in commonly owned United States Patent Application Serial No. 09/500,717, filed on February 9, 2000, and entitled "Coated Conductor Thick Film Precursor," which is hereby incorporated by reference in its entirety.

In particular embodiments, methods can be employed to minimize the formation of undesirable a-axis oriented oxide layer grains, by inhibiting the formation of the oxide layer until the required reaction conditions are attained.

Conventional processes developed for decomposition and reaction of fluoride-containing precursors use a constant, and low, non-turbulent flow of process gas that is introduced into the decomposition furnace in an orientation that is parallel to the film surface, resulting in a stable boundary layer at the film/gas interface. In the apparatus types typically used for oxide layer precursor decomposition and reaction, the diffusion of gaseous reactants and products through this gas/film boundary layer appears to control the overall reaction rates. In thin, small area films (for example, less than about 0.4 microns thick and less than about a square centimeter), the diffusion of H_2O into the film and the diffusion of HF out of the film occur at rates such that the formation of the $YBa_2Cu_3O_{7-x}$ phase does not begin at any significant rate until the sample reaches the processing temperature. However, as the film thickness or area increases, the rates of gaseous diffusion into and out of the film decrease, all other parameters being equal. This results in longer reaction times and/or incomplete formation of the $YBa_2Cu_3O_{7-x}$ phase, resulting in reduced crystallographic texture, lower density, and reduced critical current density. Thus, the overall rate of $YBa_2Cu_3O_{7-x}$ phase formation is determined, to a significant extent, by the diffusion of gases through the boundary layer at the film surface.

One approach to eliminating these boundary layers is to produce a turbulent flow at the film surface. Under such conditions, the local gas composition at the interface is maintained essentially the same as in the bulk gas (that is, the pH_2O is constant, and the pHF is approximately zero). Thus, the concentration of the gaseous products/reactants in the film is not controlled by the diffusion through the gas/film surface boundary layer condition, but rather by diffusion through the film. In order to minimize the nucleation of a-axis $YBa_2Cu_3O_{7-x}$ oriented grains on a substrate surface, the formation of the $YBa_2Cu_3O_{7-x}$ phase is inhibited until desired process conditions are reached. For example, the formation of the $YBa_2Cu_3O_{7-x}$ phase can be inhibited until desired process temperature is reached.

In one embodiment, a combination of: 1) low (non-turbulent) process gas flow, so that a stable boundary layer is established at the film/gas interface, during the ramp to temperature, and 2) high (turbulent) process gas flow, so that the boundary layer is disrupted at the film/gas interface, is employed. For example, in a three inch
5 tube furnace, the flow can be from about 0.5 to about 2.0 L/min during the temperature ramp from ambient temperature to the desired process temperature. Thereafter, the flow can be increased to a value of from about 4 to about 15 L/min during the time at which the film is being processed. Thus, the rate of formation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and epitaxial texture formation can be increased at high temperature,
10 while minimizing the amount of unwanted a-axis nucleation and growth at low temperature during ramp up. According to these processes, a-axis nucleated grains are desirably present in an amount of less than about 1%, as determined by scanning electron microscopy.

More details are provided in commonly owned U.S. Patent Application Serial
15 No. _____, filed on even date herewith, and entitled "Control of Oxide Layer Reaction Rates," which is hereby incorporated by reference.

In preferred embodiments of the present invention, cap layer 20 is deposited on layer 18. Cap layer 20 can be formed of one or more layers. Cap layer 20 preferably includes at least one noble metal layer. "Noble metal", as used herein, is a
20 metal whose reaction products are thermodynamically unstable under the reaction conditions employed to prepare the HTS tape. Exemplary noble metals include for example silver, gold, palladium and platinum. Noble metals provide a low interfacial resistance between the HTS layer and the cap layer. In addition, cap layer 20 can include a second layer of normal metal (for example, Cu or Al or alloys of normal
25 metals).

Decomposition of precursor alkoxide solutions directly on metal substrates carried out entirely under reducing atmospheres (relative to the metal substrate) can result in epitaxial metal oxide layer formation for buffer layers. However, the resulting films generally suffer from two recognized complications: 1) such films
30 have been observed to include incompletely covered grain boundaries of the substrate; and 2) such films generally contain significant levels of carbon-containing

contaminants, presumably arising from the carbon containing constituents of the precursors (e.g., the alkoxide ligands of an RE(OR)_3 precursor).

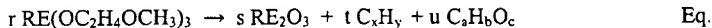
Complete coverage of metal substrates, including grain boundaries, can be ensured by providing complete wetting of the substrate surface, including the grain
5 boundaries, by a precursor solution.

According to particular embodiments, heating of a sol gel precursor film is carried out, allowing the precursor to flow into the grain boundary areas, resulting in complete coverage. The heating can be relatively low temperature, for example, from about 80°C to about 320°C, for example, from about 100°C to about 300°C, or from
10 about 100°C to about 200°C. Such temperatures can be maintained from about 1 to about 60 minutes, for example, from about 2 to about 45 minutes, or from about 15 to about 45 minutes. In a particular embodiment, heating to a temperature of 120°C for about 30 minutes was sufficient to achieve virtually complete coverage of grain boundaries. The heating step can also be carried out using higher temperatures for a
15 shorter time, for example, a film can be processed within two minutes at a temperature of 300°C. In preferred embodiments, there is virtually no difference between the degree of coverage of the surface grains and the grain boundaries, as detected by a surface visualization technique, such as scanning electron microscopy. Further, in preferred embodiments, at least about 90% of the grain boundaries are
20 covered by the oxide layer, more preferably at least about 95%, and even more preferably, at least about 99% of the grain boundaries are covered by the oxide layer.

This heating step can be carried out after, or concurrently with, the drying of excess solvent from the sol gel precursor film. It must be carried out prior to decomposition of the precursor film, however.

25 The carbon contamination accompanying conventional oxide film preparation is believed to be the result of an incomplete removal of the organic components of the precursor film. While not bound by any particular theory of operation, it appears likely that under the reducing conditions employed for the processing of the precursor solution, organic components are at least partially reduced and remain in the film.
30 Typical reducing conditions for nickel are the use of a process gas including 4% H_2 in

a carrier gas such as argon or nitrogen at a temperature of from about 500° to about 1200° C. Such reactions are referred to in Eq. 1.



where RE is a rare earth, as defined herein, and x, y, a, b, c, r, s, t and u are numbers, including zero, required to balance the material on either side of the reaction arrow.

The presence of carbon-containing contaminants C_xH_y and $\text{C}_8\text{H}_8\text{O}_6$ in or near the oxide layer can be detrimental, since they can alter the epitaxial deposition of subsequent oxide layers. Additionally, it is likely that the trapped carbon-containing contaminants buried in the film can be oxidized during the processing steps for subsequent oxide layers, which can utilize oxidizing atmospheres. The oxidation of the carbon-containing contaminants can result in CO_2 formation, and the subsequent blistering of the film, and possible delamination of the film, or other defects in the composite structure. Thus, it is undesirable to allow carbon-containing contaminants arising from metal alkoxide decomposition to become oxidized only after the oxide layer is formed. Preferably, the carbon-containing contaminants are oxidized (and hence removed from the film structure as CO_2) as the decomposition occurs. Also the presence of carbon-containing species on or near film surfaces can inhibit the epitaxial growth of subsequent oxide layers. In preferred embodiments, the carbon content of the oxide film is less than about ____.

To ensure oxidation of carbon-containing contaminants as the precursor solution decomposes into an oxide layer film, the oxygen content of the process gas can be increased. However, in the presence of process gas containing significant levels of oxygen, some rare earth oxide films form with a significant and undesirable amount of [222] texture, rather than a desired [400] structure, as shown in Fig. 2. Other materials, perovskites, may form undesirable [111] texture, at the expense of desired [200] structure, as recognized by those of skill in the art. In

preferred embodiments, at least about 95% of the surface is coated with the desired texture, more preferably, at least about 98% of the surface is coated with the desired texture.

According to particular embodiments, after coating a metal substrate or buffer layer, the precursor solution can be air dried, and then heated in an initial decomposition step. Alternatively, the precursor solution can be directly heated in an initial decomposition step, under an atmosphere that is reducing relative to the metal substrate. Generally, the procedures are carried out at approximately 1 atmosphere pressure, although pressures can range from about 0.75 to about 1.25 atmospheres. Fig. 3 shows the stability line for Ni/NiO and Cu/CuO as a function of temperature and partial oxygen pressure. Thus, for example, a suitable atmosphere for initial decomposition on a nickel substrate is 4% H₂ in an inert carrier gas such as argon or nitrogen. Such gas may not be appropriate for particular alloys, such as nickel-chromium, or copper-nickel-aluminum, which contain an element that would oxidize in this atmosphere at temperatures used for decomposition. Such alloys may require the use of a transient layer, as described herein for particular embodiments.

Once the oxide layer initially nucleates on the metal substrate in the desired epitaxial orientation, the oxygen level of the process gas is increased, for example, by adding water vapor or oxygen. In some embodiments, water vapor is added to the process gas, for example from about 0.5% to about 10%, or from about 0.5% to about 5%, for example, 2.2% water vapor at room temperature (approximately saturation conditions). Water vapor in the presence of hydrogen can establish an equilibrium with oxygen, in a temperature dependent equilibrium, as is recognized by those of skill in the art. The oxide layer nucleation step requires from about 1 minute to about 30 minutes to take place under typical conditions, and is generally temperature dependent. For example, at about 1150°C, nucleation can begin to take place in from about 1 to about 5 minutes, and at about 1000°C, nucleation can begin to take place in from about 5 to about 10 minutes.

The initial decomposition step, under reducing atmosphere, can be carried out as a step distinct from the post-nucleation decomposition, under more oxidizing atmosphere. Alternatively, the process steps can be carried out as a combined

procedure. For example, a continuous process can be developed in which a substrate passes from an area of reducing conditions (with respect to the substrate) to less reducing conditions (with respect to the substrate).

5 The use of process gases of different reduction potential for initial decomposition and decomposition taking place after nucleation results in a reduction in the carbon content of the resulting oxide layer film. Epitaxial structure also results from this procedure.

10 In some embodiments, multi-layer high temperature superconductors are provided, including first and second high temperature superconductor coated elements. Each element includes a substrate, at least one buffer layer deposited on the substrate, a high temperature superconductor layer, and a cap layer. The first and second high temperature superconductor coated elements are joined at the first and second cap layers. Exemplary joining techniques include soldering and diffusion bonding.

15 Such a multi-layer architecture provides improved current sharing, lower hysteretic losses under alternating current conditions, enhanced electrical and thermal stability, and improved mechanical properties. Useful conductors can be made having multiple tapes stacked relative to one another and/or laminated to provide sufficient ampacity, dimensional stability, and mechanical strength. Such embodiments also
20 provide a means for splicing coated tape segments and for termination of coated tape stackups or conductor elements.

Moreover, it is expected that this architecture can provide significant benefits for alternating current applications. AC losses are shown to be inversely proportional to the effective critical current density within the conductor, more specifically, the
25 cross-sectional area within which the current is carried. For a multifilamentary conductor, this would be the area of the "bundle" of superconducting filaments, excluding any sheath material around that bundle. For a "face-to-face" architecture, the "bundle" critical current density would encompass only the high temperature superconductor films and the thickness of the cap layer structure. The cap layer can
30 be formed of one or more layers, and preferably includes at least one noble metal

layer. "Noble metal," as used herein, is a metal, the reaction products of which are thermodynamically unstable under the reaction conditions employed to prepare the HTS tape. Exemplary noble metals include, for example, silver, gold, palladium, and platinum. Noble metals provide a low interfacial resistance between the HTS layer and the cap layer. In addition, the cap layer can include a second layer of normal metal (for example, copper or aluminum or alloys of normal metals). In direct current applications, additional face-to-face wires would be bundled or stacked to provide for the required ampacity and geometry for a given application.

Additionally, the high temperature superconductor film on the surface of the tapes could be treated to produce local breaks, that is, non-superconducting regions or stripes in the film only along the length of the tape (in the current flow direction). The cap layer deposited on the high temperature superconductor film would then serve to bridge the nonsuperconducting zones with a ductile normal metal region. An offset in the edge justification of the narrow strips or filaments, similar to a running bond brick pattern, would allow current to transfer to several narrow superconducting filaments both across the cap layers and to adjacent filaments, further increasing the redundancy and improving stability.

In all embodiments, a normal metal layer could be included along the edge of the conductor to hermetically seal the high temperature superconductor films and to provide for current transfer into the film, and if necessary, from the film into the substrate.

In particular embodiments, tensile strain on the superconducting layers can be minimized by providing the superconducting layer within a neutral mechanical axis zone. A "neutral mechanical axis" of a flexible material in the form of a tape of layered materials is a plane in the plane of the tape, coplanar with the layers of the tape, in which tensile strain experienced upon bending the material in a direction normal to the plane is zero. An operational layer centered on this axis will experience minimum tensile strain. A "neutral mechanical axis zone" is a region where the maximum strain experienced by the superconducting layer is less than that which would lead to degraded performance. The criterion for positioning the operational layer within the neutral mechanical axis zone is derived by balancing the moments in

bending. This is done by properly specifying the thicknesses, positions, and Young's modulus of the laminate layer or layers; laminate layers are those layers which are non-operational, and can include substrate, buffer and cap layers, for example.

5 More details are provided in commonly owned U.S. Provisional Patent Application Serial No. 60/145,458, filed on July 23, 1999, and entitled "Enhanced High Temperature Coated Superconductors," and commonly owned United States Patent Application Serial No. _____, filed concurrently herewith, and entitled "Enhanced High Temperature Coated Superconductors," both of which are hereby incorporated by reference in its entirety.

10 In some embodiments, coated conductors can be fabricated in a way that minimizes losses incurred in alternating current applications. The conductors are fabricated with multiple conducting paths, each of which comprises path segments which extend across at least two conducting layers, and further extend between these layers.

15 Each superconducting layer has a plurality of conductive path segments extending across the width of the layer, from one edge to another, and the path segments also have a component of direction along the length of the superconducting layer. The path segments in the superconducting layer surface are in electrically conductive communication with interlayer connections, which serve to allow current
20 to flow from one superconducting layer to another. Paths, which are made up of path segments, are periodically designed, so that current flow generally alternates between two superconducting layers in bilayered embodiments, and traverses the layers through interlayer connections.

25 Superconducting layers can be constructed to contain a plurality of path segments which extend both across their widths and along their lengths. For example, superconducting layers can be patterned so as to achieve a high resistivity or a fully insulating barrier between each of the plurality of path segments. For example, a regular periodic array of diagonal path segments can be imposed on the layer along the full length of the tape. Patterning of superconducting layers to give such arrays
30 can be accomplished by a variety of means known to those skilled in the art, including

for example, laser scribing, mechanical cutting, implantation, localized chemical treatment through a mask, and other known methods. Further, the superconducting layers are adapted to allow the conductive path segments in their surfaces to electrically communicate with conducting interlayer connections passing between the layers, at or near their edges. The interlayer connections will typically be normally conducting (not superconducting) but in special configurations could also be superconducting. Interlayer connections provide electrical communication between superconducting layers which are separated by non-conducting or highly resistive material which is positioned between the superconducting layers. Such non-conducting or highly resistive material can be deposited on one superconducting layer. Passages can be fabricated at the edges of the insulating material to allow the introduction of interlayer connections, followed by deposition of a further superconducting layer. One can achieve a transposed configuration with coated conductors by patterning a superconducting layer into filaments parallel to the axis of the tape and winding the tape in a helical fashion around a cylindrical form.

More details are provided in commonly owned United States Patent Application Serial No. 09/500,718, filed on February 9, 2000, and entitled "Coated Conductors with Reduced AC Loss," which is hereby incorporated by reference in its entirety.

The invention will be further described in the following examples, which do not limit the scope of the invention described in the claims.

EXAMPLES

Example 1: Uncovered Grain Boundaries

Example 1 illustrates a general procedure for determining the extent and type of texture present on a tape surface.

A Gd_2O_3 precursor was deposited on a deformation textured Ni tape with a 1-cm width using a reel-to-reel slot die coater. The Gd_2O_3 precursor included a solution of $\text{Gd}(\text{OC}_2\text{H}_4\text{OCH}_3)_3$ in 2-methoxyethanol. The concentration of the solution was 0.8 M Gd. The Ni tape was prepared by rolling a nickel strip (+99.95% purity) to a thickness of between about 0.1" and 0.3" and annealing to obtain a smaller grain size,

typically 20-200 micron average. The strip was rolled to an additional reduction of >95%, slit to the desired width, degreased, and texture annealed using a continuous or batch anneal in an argon/hydrogen mixture ("forming gas"), at temperatures of 700-1200°C.

5 The precursor solution was deposited over the Ni tape with a thickness equivalent to 0.5 gm $\text{Gd}_2\text{O}_3/\text{m}^2$ of Ni. The coated tape was dried at ambient temperature ($\sim 23^\circ\text{C}$) in an atmosphere with a relative humidity of <30%RH. The short length of the Ni tape containing the dried precursor film was cut and was then heated to 1150° at a rate of $75\text{-}100^\circ\text{C}/\text{min}$ in a flowing argon atmosphere (1 atm total
10 pressure) containing 4% H_2 . The sample was held at 1150°C for 30 minutes and cooled to room temperature in the same atmosphere. An x-ray diffraction analysis of films prepared according to this example showed that the Gd_2O_3 formed epitaxially on the Ni substrate. The 2-theta x-ray scan of a representative film prepared according to this example is shown in Fig. 4, which shows the c-axis orientation of the film. Pole
15 figure analysis also confirms the plane orientation of the Gd_2O_3 film, as shown in Fig. 5.

Scanning electron microscope analysis of a representative Gd_2O_3 film prepared according to the procedures of this example is shown in Fig. 6, which shows that Gd_2O_3 formed uniformly over the surface of the Ni grains of the deformation textured
20 substrate. However, the Gd_2O_3 did not completely cover the grain boundaries in the Ni substrate.

Example 2: Covered Grain Boundaries

25 A Gd_2O_3 precursor was deposited on a deformation textured Ni substrate and dried at ambient temperature as described in Example 1. Prior to processing the precursor at 1150°C , the sample was heated to 120°C for 60 minutes in room air. The sample was then reacted to the Gd_2O_3 phase as described in Example 1. X-ray analysis of representative films prepared according to Example 2 showed the formation of an epitaxial Gd_2O_3 film. SEM micrograph in Fig. 7 shows that the grain

boundaries were completely covered by a representative Gd_2O_3 film prepared according to the procedures of this example.

Example 3: Covered Grain Boundaries

5 A Gd_2O_3 precursor, as described in Example 1, was deposited on a deformation textured Ni substrate using a slot die coater. Immediately after the precursor coating was deposited, the tape was passed through an oven at a temperature of 300°C in an atmosphere of dry air. The coated tape remained in the 300°C zone of the oven for two minutes. The Ni tape, containing the dried precursor film, was then transported, using a reel-to-reel system, through an 1150°C zone of the
10 oven. X-ray analysis confirmed the epitaxial formation of the Gd_2O_3 film on the deformation textured Ni substrate. SEM analysis confirmed that the Gd_2O_3 film covered the grain boundaries of the Ni substrate.

Example 4: Carbon Contaminated Films

A Gd_2O_3 film was prepared on a deformation textured Ni substrate as
15 described in Example 3. Rutherford backscatter (RBS) analysis of the film showed that the presence of a carbon contamination in the Gd_2O_3 film as seen in Fig. 8, curve A.

Example 5: Carbon Uncontaminated Films

A Gd_2O_3 film was prepared as described in Example 4. The Ni tape
20 containing the Gd_2O_3 film was then transported, using a reel-to-reel system, through an oven at a temperature of 1150°C with a flowing atmosphere (1 atmosphere total pressure) of argon containing 4% H_2 and 2.2% H_2O . The tape was transported at a rate sufficient to allow a residence time of 15 minutes in the 1150°C zone of the oven. RBS analysis of the film shown in Fig. 8, curve B shows that minimal or no
25 detectable carbon contamination remains in the Gd_2O_3 film.

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the forgoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the
30 scope of the following claims.

What is claimed is:

1. A method of making an oxide layer, the method comprising:
 - 1) coating a biaxially textured surface with a precursor comprising rare earth alkoxides and a solvent;
 - 5 2) removing the solvent;
 - 3) heating the coated surface to a first temperature for a first time, which is sufficient to attain substantially complete coverage of grain boundaries of the surface;
 - 4) heating the coated surface, under conditions relatively reducing with respect to the surface, to a second temperature, which is sufficient to initiate nucleation of the
 - 10 oxide layer; and
 - 5) modifying the conditions to be more oxidizing with respect to the surface to form the oxide layer.
2. The method of claim 1, wherein the first temperature is between about 80 and about 320 °C.
- 15 3. The method of claim 2, wherein the first temperature is between about 100 and 300°C.
4. The method of claim 3, wherein the first temperature is between about 100 and 200°C.
5. The method of claim 1, wherein the first time is between about 1 and
- 20 about 60 minutes.
6. The method of claim 5, wherein the first time is between about 2 and about 45 minutes.
7. The method of claim 6, wherein the first time is between about 15 and about 45 minutes.
- 25 8. The method of claim 1, wherein the first temperature is about 120°C and the first time is about 30 minutes.
9. The method of claim 1, wherein the first temperature is about 300°C and the first time is about two minutes.

10. The method of claim 1, wherein steps 2 and 3 are carried out substantially simultaneously.
11. The method of claim 1, wherein the biaxially textured surface is a metal or metal alloy substrate.
- 5 12. The method of claim 11, wherein the metal or metal alloy substrate comprises nickel.
13. The method of claim 1, wherein the biaxially textured surface is at least one metal oxide buffer layer coating a metal or metal alloy substrate.
14. The method of claim 13, wherein the metal oxide buffer layer
10 comprises cerium oxide.
15. The method of claim 13, wherein the metal oxide buffer layer comprises gadolinium oxide.
16. The method of claim 13, wherein the metal oxide buffer layer comprises at least one of CeO_2 , Y_2O_3 , Yb_2O_3 , Gd_2O_3 , Eu_2O_3 , SrTiO_3 , LaAlO_3 ,
15 GdCuO , or LaNiO_3 .
17. The method of claim 1, wherein the conditions relatively reducing with respect to the surface comprise exposure to a gas comprising from about 1 to about 20% hydrogen.
18. The method of claim 16, wherein the conditions relatively reducing
20 with respect to the surface comprise exposure to a gas comprising from about 2 to about 6% hydrogen.
19. The method of claim 1, wherein the second temperature is from about 600°C to about 1200°C.
20. The method of claim 18, wherein the second temperature is from about
25 800°C to about 1150°C.
21. The method of claim 1, wherein modification of the conditions comprises exposure to a gas comprising from about 2 to about 6% H_2 , and from about 0.5 to about 5% water vapor.

22. The method of claim 1, wherein the duration of step 4) is from about 1 to about 60 minutes at about 1150°C.
23. An article formed according to the method of claim 1.
24. A coated biaxially textured surface comprising grains and grain boundaries, wherein the surface is coated with an oxide layer, wherein the coating takes place with a dry process gas, and wherein the degree of grain coating and the degree of grain boundary coating is substantially the same, as detected by scanning electron microscopy.
25. The surface of claim 24, wherein less than about 10% of grain boundaries are not coated with an oxide layer.
26. The surface of claim 25, wherein less than about 5% of grain boundaries are not coated with an oxide layer.
27. The surface of claim 26, wherein less than about 1% of grain boundaries are not coated with an oxide layer.
28. The surface of claim 24, wherein at least about 95% of the surface is coated with a desired texture.
29. The surface of claim 28, wherein at least about 98% of the surface is coated with a desired texture.
30. The surface of claim 24, wherein the carbon content of the oxide layer is reduced relative to the carbon content of the oxide layer produced without wet process gas.

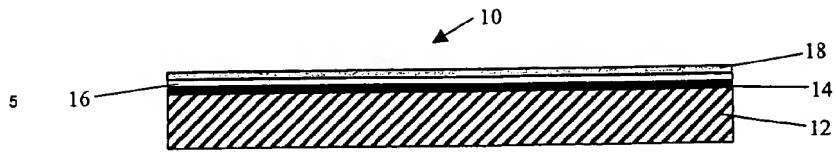


Fig. 1

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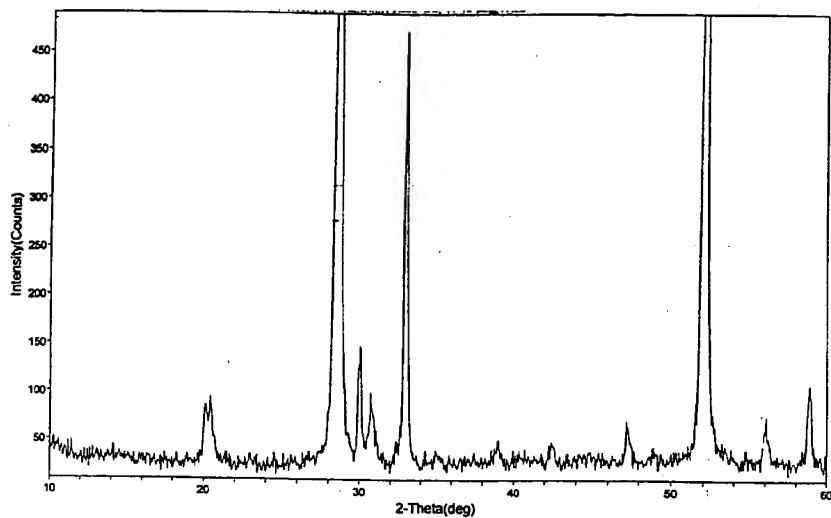


Fig. 2

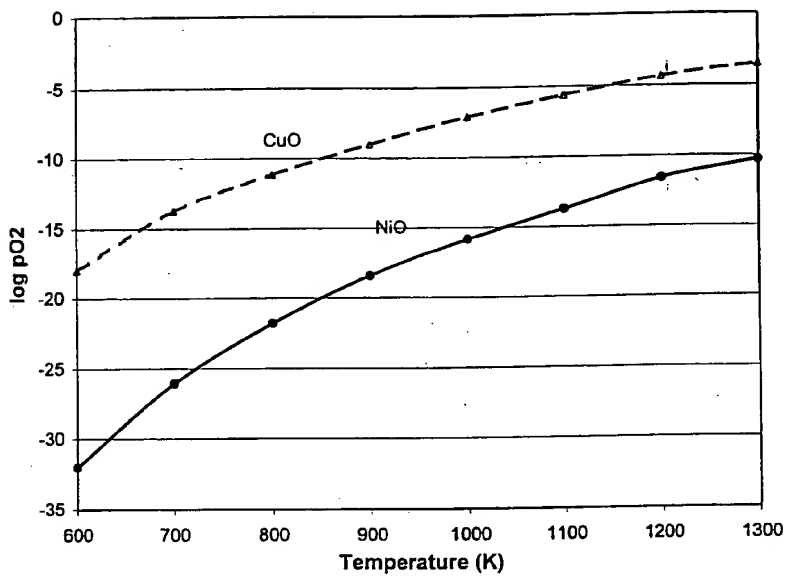


Fig. 3

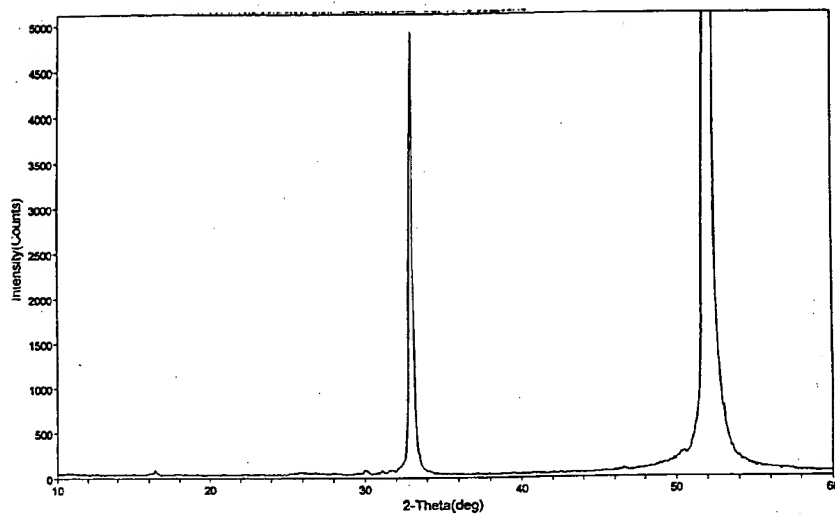


Fig. 4

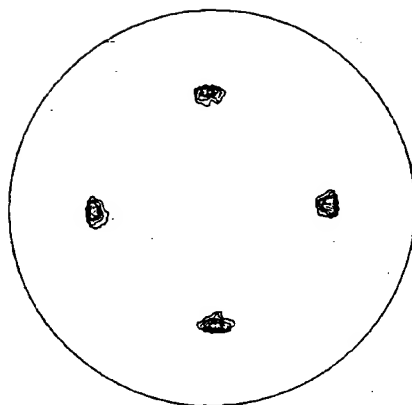
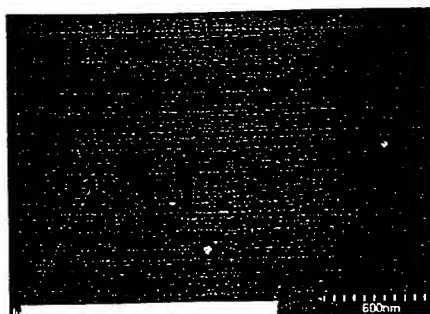


Fig. 5



Ni Grain Boundary

Fig. 6



Ni Grain Boundary

Fig 7

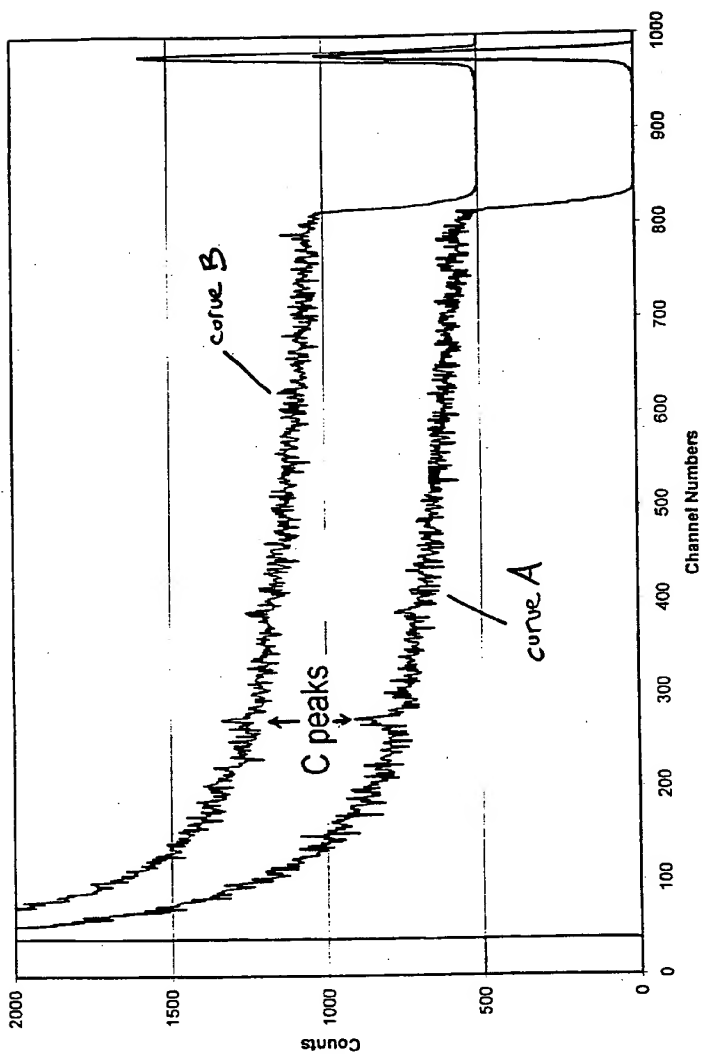


Fig. 8